

Nanostructured Electrode Materials made by Combustion Synthesis

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Combustion synthesis techniques may be used to prepare high-quality nano-particulate electrode materials for use in lithium ion batteries. Either phase-pure oxides and phosphates or carbon-containing composites may easily be prepared in a one-step process. The composites may contain carbon nanotubes or fibers as separate entities or may consist of carbon-coated particles of active material.

In general, nitrate and/or phosphate precursors are used in combination with an appropriate fuel such as glycine or citric acid. The combustion temperature is determined by the fuel:nitrate ratio, which can be varied over a wide range. Temperatures as high as 1400°C may be realized. This allows the production of high quality carbon (i.e., with graphitic characteristics) not normally achievable during conventional synthesis at lower temperatures. Due to the rapidity of the reaction, the thermodynamically favored product may not be produced initially. XRD analysis of the ash often shows that it is amorphous or only partially crystalline, but a brief calcination causes crystallization to occur and the desired phase is produced. Carbon content is determined both by the type of fuel and the amount. Glycine usually results in very little residual carbon, whereas citric acid is suitable for the production of phosphates such as olivines because carbon is co-produced during the initial combustion. This is useful because it avoids a second step in which carbon is added and the mixture then processed.

We have succeeded in making a series of partially Al-substituted layered mixed transition metal oxides via combustion synthesis. These compounds can be difficult to make by the more familiar mixed hydroxide route due to problems with homogeneity and the production of aluminum oxides as impurities. Using combustion techniques, single phase materials can be made up to about $y=0.2$ for the series $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}]\text{O}_2$ and $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Al}_y\text{Mn}_{1/3}]\text{O}_2$. Compounds with low levels of Al substitution have similar practical capacities as analogs with no Al, but rate capabilities are improved, suggesting that the increased homogeneity results in better electrochemical properties.

Composites of carbon and olivines such as LiFePO_4 and LiMnPO_4 can also be made easily. This is particularly advantageous in the case of the latter, which normally shows very poor electrochemical properties due to its low conductivity. The extremely small size of the particles (~30 nm) and the co-production of high quality carbon during combustion are beneficial to the performance. A particular challenge, however, is the need to produce samples with little agglomeration and even dispersion of carbon to ensure full utilization.

$\text{Na}_{0.44}\text{MnO}_2$ and $\text{Na}_{0.44}\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ ($0 \leq y \leq 0.55$) compounds can also be produced by combustion. These materials can be used as is in battery or supercapacitor configurations, or ion-exchanged for use in lithium batteries. Ion conduction is anisotropic, occurring along tunnels that are aligned parallel to the long axes of the needle-shaped particles. The smaller needles produced by combustion, compared to conventional solid-state synthesis, result in materials with higher rate capability as a consequence of the shorter diffusion pathlength.

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